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Syntheses, Crystal Structures, and Some Spectrochemical Properties of S-Bridged Tetranuclear Complexes with Stacking Arrangements Composed of Planar Palladium(II) Units

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The reaction of $[Pd(aet)_2]$ (aet = 2-aminoethanethiolate) with $[Pd(NO_3)_2(diimine)]$ (diimine = 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (dmbpy), 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (dmphen)) gave a new type of S-bridged tetranuclear complex $[\{Pd(diimine)\}_2\{Pd(aet)_2\}_2]^{4+}$. The crystal structures of these complexes were determined by X-ray crystallography. In these complexes, the two intramolecular diimine moieties are aligned so as to overlap each other and the PdN_2S_2 planes in the $\{Pd(aet)_2\}$ units are almost perpendicular to those in the $\{Pd(diimine)\}$ moieties. In the case of diimine = bpy and dmbpy, furthermore, the complex cations exist in the dimeric structure with a coplanar stacking arrangement, in which the diimine moieties of the two distinct complex cations are antiparallel to each other. In the case of diimine = phen and dmphen, on the other hand, the complex cations exist in the linear-chain-like structure with an alternate coplanar stacking arrangement, in which the diimine moieties of the neighboring complex cations are antiparallel to each other. All of the complexes were characterized on the basis of the electronic absorption, diffuse reflection, and ^{13}C NMR spectra.

The square-planar $[M(thiolato\text{-}S)_2(amine\text{-}N)_2]$-type complexes, such as $[M(aet)_2]$ (M = Ni^{II}, Pd^{II}, aet = 2-aminoethanethiolate), which have two available sulfur atoms for bridging other metal ions and can function as bidentate metalloligands, have been used for constructions of S-bridged polynuclear complexes with square-planar geometry.[1—14] It is known that such type of metalloligand retains its square-planar geometry before and after the reactions with other metals.[1,2,14] In the case of the reaction of $[Ni(aet)_2]$ with Ni(II) ion, for instance, a linear-type S-bridged trinuclear complex, $[Ni\{Ni(aet)_2\}]^{2+}$, in which each of two square-planar *cis(S)*-$[Ni(aet)_2]$ units spans to one Ni(II) ion, is formed.[1,2] On the other hand, the reaction between $[Pd(aet)_2]$ and Pd(II) ion gives a pin-wheel-type S-bridged hexanuclear complex, $[Pd_2\{Pd(aet)_2\}_4]^{4+}$, in which each of four square-planar *cis(S)*-$[Pd(aet)_2]$ units spans two Pd(II) ions.[14] Taking into account these facts, we expected that the dinuclear complexes, $[M'(diimine)\ \{M(aet)_2\}]^{2+}$ (M′ = Pd^{II} or Pt^{II}, diimine = 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (dmbpy), 1,10-phenanthroline (phen), etc.), or tetranuclear ones, $[\{M'(diimine)\}_2\{M(aet)_2\}_2]^{4+}$, would be obtained from the reactions of $[M(aet)_2]$ with $[M'X_2(diimine)]$ (X = Cl, NO_3, H_2O, etc.), in which the diimine ligands are less susceptible to substitution of other ligands. The square-planar d^8 metal complexes with aromatic diimine ligands sometimes exist as stacking forms due to π-π interactions;[15—19] thus, such reactions would bring about construction of polynuclear complexes with intramolecular stacking arrangement, namely the latter tetranuclear complexes, $[\{M'(diimine)\}_2\{M(aet)_2\}_2]^{4+}$. However, it has been shown that the square-planar $[Ni(aet)_2]$ reacts with $[M'Cl_2(bpy)]$ to form unexpected dinuclear complexes, $[M'(bpy)\{Ni(aet)_2(H_2O)_2\}]^{2+}$, in which the Ni(II) ion is converted from the square-planar coordination geometry to the octahedral one.[20] In order to follow up the constructions of $[M'(diimine)\{M(aet)_2\}]$- or $[\{M'(diimine)\}_2\{M(aet)_2\}_2]$-type complexes, therefore, the reactions using metalloligands such as $[Pd(aet)_2]$, in which Pd(II) ion more tightly takes square-planar geometry than Ni(II) ion, are required. Recently, we have reported a preliminary result that the reaction of $[Pd(aet)_2]$ with $[Pd(NO_3)_2(bpy)]$ gives an expected tetranuclear complexes, $[\{Pd(bpy)\}_2\{Pd(aet)_2\}_2]^{4+}$, in which two bpy moieties are aligned so as to overlap each other and take intramolecular stacking arrangement.[21] In the crystalline state, furthermore, the complex exists as dimeric form with a coplanar stacking arrangement, in which the bpy moieties of the two distinct complex cations are antiparallel to each other. In the present paper, we report on a detailed study concerning the syntheses, structures, and some spectrochemical properties of the S-bridged tetranuclear complexes, $[\{Pd(diimine)\}_2\{Pd(aet)_2\}_2]^{4+}$ (diimine; bpy (**1**), dmbpy (**2**), phen (**3**), 4,7-dimethyl-1,10-phenanthroline = dmphen (**4**)).

Experimental

Materials. Na_2PdCl_4 and $Pd(NO_3)_2$ were purchased from Tanaka Rare Metal Industries Ltd., and Wako Pure Chemical Ind. Co., Ltd., respectively. 2,2'-Bipyridine and 1,10-phenanthroline are obtained from Wako Pure Chemical Ind. Co., Ltd., and 4,4′-dimethyl-2,2′-bipyridine and 4,7-dimethyl-1,10-phenanthroline from Aldrich Chemical Co., Inc. The mononuclear complexes, [Pd-

$(NO_3)_2$(diimine)] and [Pd(aet)$_2$], were prepared by the modified methods from the literature.[1,23] The other chemicals were purchased from Wako Pure Chemical Ind. Co., Ltd. or Tokyo Chemical Co., Ltd. All of the chemicals were of reagent grade and were used without further purification.

Preparation of Complexes. **[{Pd(bpy)}$_2${Pd(aet)$_2$}$_2$]-$(NO_3)_4\cdot 5H_2O$ (1$(NO_3)_4\cdot 5H_2O$).** To a yellow suspension containing 0.26 g (1.0 mmol) of [Pd(aet)$_2$] in 20 cm^3 of water was added 0.40 g (1.0 mmol) of [Pd$(NO_3)_2$(bpy)].[1,22] The mixture was stirred at 50 °C for 1 d, whereupon the mixture became a yellowish orange solution. After cooling to room temperature, any unreacted materials were removed by filtration. A few drops of a saturated $NaNO_3$ solution were added to the yellowish orange filtrate. The mixture was allowed to stand at 4 °C for several days, and the resulting yellowish orange crystals were collected by filtration. A well-formed crystal of **1**$(NO_3)_4\cdot 5H_2O$ was used for the X-ray analysis. ^{1}H NMR (500 MHz, D_2O) δ = 2.88 (m, 4H, aet), 3.00 (m, 4H, aet), 3.22 (m, 4H, aet), 7.64 (t, 4H, bpy), 8.04 (t, 4H, bpy), 8.10 (d, 4H, bpy), 9.00 (d, 4H, bpy); ^{13}C NMR (500 MHz, D_2O) δ = 38.42 (aet), 50.29 (aet), 126.46 (bpy), 130.99 (bpy), 144.75 (bpy), 151.67 (bpy), 157.39 (bpy). Calcd for [{Pd(bpy)}$_2${Pd(aet)$_2$}$_2$]$(NO_3)_4\cdot 5H_2O$ = $C_{28}H_{50}N_{12}O_{17}S_4Pd_4$: C, 24.36; H, 3.65; N, 12.17%. Found: C, 24.46; H, 3.55; N, 12.11%.

[{Pd(dmbpy)}$_2${Pd(aet)$_2$}$_2$]$(NO_3)_4\cdot 3H_2O$ (2$(NO_3)_4\cdot 3H_2O$). To a yellow suspension containing 0.26 g (1.0 mmol) of [Pd(aet)$_2$] in 100 cm^3 of water was added 0.41 g (1.0 mmol) of [Pd$(NO_3)_2$(dmbpy)].[1,22] The mixture was stirred at 50 °C for 1 d, whereupon the mixture became a yellowish orange solution. After cooling to room temperature, any unreacted materials were removed by filtration. The yellowish orange crystals were obtained by slow evaporation of the filtrate at room temperature. A well-formed crystal of **2**$(NO_3)_4\cdot 3H_2O$ was used for the X-ray analysis. ^{1}H NMR (500 MHz, D_2O) δ = 2.53 (s, 12H, dmbpy), 2.86 (m, 4H, aet), 3.00 (m, 4H, aet), 3.22 (m, 4H, aet), 7.48 (d, 4H, bpy), 8.10 (s, 4H, bpy), 8.78 (d, 4H, bpy); ^{13}C NMR (500 MHz, D_2O) δ = 23.32 (dmbpy), 38.29 (aet), 50.38 (aet), 126.79 (dmbpy), 131.31 (dmbpy), 151.01 (dmbpy), 157.06 (dmbpy), 157.64 (dmbpy). Calcd for [{Pd(dmbpy)}$_2${Pd(aet)$_2$}$_2$]$(NO_3)_4\cdot 3H_2O$ = $C_{32}H_{54}N_{12}O_{15}S_4Pd_4$: C, 27.44; H, 3.89; N, 12.07%. Found: C, 27.58; H, 3.95; N, 12.01%.

[{Pd(phen)}$_2${Pd(aet)$_2$}$_2$]$(NO_3)_4\cdot 3H_2O$ (3$(NO_3)_4\cdot 3H_2O$). To a yellow suspension containing 0.26 g (1.0 mmol) of [Pd(aet)$_2$] in 20 cm^3 of water was added 0.41 g (1.0 mmol) of [Pd$(NO_3)_2$(phen)].[1,22] The mixture was stirred at 50 °C for 1 d, whereupon the mixture became a yellowish orange solution. After cooling to room temperature, any unreacted materials were removed by filtration. The filtrate was allowed to stand at 4 °C for several days, and the resulting yellowish orange fine crystals were collected by filtration. ^{1}H NMR (500 MHz, D_2O) δ = 2.91 (m, 4H, aet), 3.09 (m, 4H, aet), 3.28 (m, 4H, aet), 7.70 (q, 4H, phen), 7.78 (s, 4H, phen), 8.41 (d, 4H, phen), 9.08 (d, 4H, phen); ^{13}C NMR (500 MHz, D_2O) δ = 38.58 (aet), 50.46 (aet), 129.00 (phen), 130.34 (phen), 132.47 (phen), 143.55 (phen), 146.59 (phen), 151.94 (phen). Calcd for [{Pd(phen)}$_2${Pd(aet)$_2$}$_2$]$(NO_3)_4\cdot 3H_2O$ = $C_{32}H_{46}N_{12}O_{15}S_4Pd_4$: C, 27.60; H, 3.33; N, 12.07%. Found: C, 27.61; H, 3.25; N, 11.89%.

[{Pd(phen)}$_2${Pd(aet)$_2$}$_2$]$(NO_3)_2SiF_6\cdot 9H_2O$ (3$(NO_3)_2SiF_6\cdot 9H_2O$). After the yellowish orange solution obtained by the same method as **3**$(NO_3)_4\cdot 3H_2O$ was cooled to 50 °C, 80 cm^3 of water and 0.18 g (1.0 mmol) of $(NH_4)_2SiF_6$ were added. After this mixture was cooled to room temperature, any unreacted materials were removed by filtration. The yellowish orange filtrate was allowed to stand at room temperature for several days, and the resulting yellowish orange crystals were collected by filtration. A well-formed crystal of **3**$(NO_3)_2SiF_6\cdot 9H_2O$ was used for the X-ray analysis. Calcd for [{Pd(phen)}$_2${Pd(aet)$_2$}$_2$]$(NO_3)_2SiF_6\cdot 9H_2O$ = $C_{32}H_{50}N_{10}O_{17}S_4Pd_4$: C, 27.60; H, 3.73; N, 8.94%. Found: C, 27.63; H, 3.77; N, 8.88%.

[{Pd(dmphen)}$_2${Pd(aet)$_2$}$_2$]$(NO_3)_4\cdot 3H_2O$ (4$(NO_3)_4\cdot 3H_2O$). To a yellow suspension containing 0.26 g (1.0 mmol) of [Pd(aet)$_2$] in 50 cm^3 of water was added 0.44 g (1.0 mmol) of [Pd$(NO_3)_2$(dmphen)].[1,22] The mixture was stirred at 50 °C for 1 d, whereupon the mixture became a yellowish orange solution. After cooling to room temperature, any unreacted materials were removed by filtration. The filtrate was allowed to stand at 4 °C for several days, and the resulting yellowish orange fine crystals were collected by filtration. ^{1}H NMR (500 MHz, D_2O) δ = 2.75 (s, 12H, dmphen), 2.91 (m, 4H, aet), 3.14 (m, 4H, aet), 3.31 (m, 4H, aet), 7.63 (d, 4H, dmphen), 7.76 (s, 4H, dmphen), 8.93 (d, 4H, dmphen); ^{13}C NMR (500 MHz, D_2O) δ = 21.16 (dmphen), 38.52 (aet), 50.50 (aet), 126.42 (dmphen), 129.32 (dmphen), 131.60 (dmphen), 146.16 (dmphen), 151.32 (dmphen), 154.23 (dmphen). Calcd for [{Pd(dmphen)}$_2${Pd(aet)$_2$}$_2$]$(NO_3)_4\cdot 3H_2O$ = $C_{36}H_{54}N_{12}O_{15}S_4Pd_4$: C, 29.84; H, 3.76; N, 11.60%. Found: C, 29.27; H, 3.79; N, 11.49%.

[{Pd(dmphen)}$_2${Pd(aet)$_2$}$_2$](NO_3) $(SiF_6)_{1.5}\cdot 11H_2O$ (4(NO_3) $(SiF_6)_{1.5}\cdot 11H_2O$). After the yellowish orange solution obtained by the same method as **4**$(NO_3)_4\cdot 3H_2O$ was cooled to 50 °C, 80 cm^3 of water and 0.18 g (1.0 mmol) of $(NH_4)_2SiF_6$ were added. After this mixture was cooled to room temperature, any unreacted materials were removed by filtration. The yellowish orange filtrate was allowed to stand at room temperature for several days, and the resulting yellowish orange crystals were collected by filtration. A well-formed crystal of **4**$(NO_3)(SiF_6)_{1.5}\cdot 11H_2O$ was used for the X-ray analysis. Calcd for [{Pd(dmphen)}$_2${Pd(aet)$_2$}$_2$](NO_3)-$(SiF_6)_{1.5}\cdot 11H_2O$ = $C_{36}H_{70}N_{10}O_{14}F_9Si_{1.5}S_4Pd_4$: C, 29.33; H, 4.79; N, 9.50%. Found: C, 29.22; H, 4.85; N, 9.39%.

Measurements. The electronic absorption and diffuse reflection spectra were recorded with a JASCO Ubest V-560 or V-570 spectrophotometer at room temperature. The ^{13}C NMR spectra were recorded with a Bruker AM-500 NMR spectrometer in D_2O. The sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as an internal reference. The nitrate salts of the complexes (**1**$(NO_3)_4\cdot 5H_2O$, **2**$(NO_3)_4\cdot 3H_2O$, **3**$(NO_3)_4\cdot 3H_2O$, and **4**$(NO_3)_4\cdot 3H_2O$) were used for these spectral measurements, because the salts containing hexafluorosilicates (**3**$(NO_3)_2SiF_6\cdot 9H_2O$ and **4**$(NO_3)(SiF_6)_{1.5}\cdot 11H_2O$), whose structures were determined by X-ray diffractions, were less soluble into water and D_2O. The elemental analyses (C, H, N) were performed by the Analysis Center of the University of Tsukuba.

Crystallography. The unit-cell parameters and intensity data for **1**$(NO_3)_4\cdot 5H_2O$, **2**$(NO_3)_4\cdot 3H_2O$, **3**$(NO_3)_2SiF_6\cdot 9H_2O$, and **4**$(NO_3)(SiF_6)_{1.5}\cdot 11H_2O$ were used for data collection on a Rigaku RASA-7S four-circle diffractometer with graphite-monochromatized Mo$K\alpha$ radiation. The unit-cell parameters were determined by a least-square refinement of 25 reflections ($5° < \theta < 15°$). The crystal data and experimental parameters are listed in Table 1. The intensity data were collected by the ω–2θ scan technique, and the intensities were corrected for Lorentz and polarization. An empirical absorption correction based on a series of Ψ scans was applied. The independent reflections with $I_0 > 2\sigma(I_0)$ were used for structure determinations. The positions of the Pd and other non-H atoms were determined by a direct method. The difference Fourier maps based on these atomic positions revealed some remaining non-hydrogen atoms. The structures were refined by a full-matrix least-squares refinement on F of the positional parameters and the anisotropic

Table 1. Crystallographic Data of $\mathbf{1}(NO_3)_4\cdot 5H_2O$, $\mathbf{2}(NO_3)_4\cdot 3H_2O$, $\mathbf{3}(NO_3)_2SiF_6\cdot 9H_2O$, and $\mathbf{4}(NO_3)(SiF_6)_{1.5}\cdot 11H_2O$

	$\mathbf{1}(NO_3)_4\cdot 5H_2O$	$\mathbf{2}(NO_3)_4\cdot 3H_2O$	$\mathbf{3}(NO_3)_2SiF_6\cdot 9H_2O$	$\mathbf{4}(NO_3)(SiF_6)_{1.5}\cdot 11H_2O$
Formula	$C_{28}H_{50}N_{12}O_{17}S_4Pd_4$	$C_{32}H_{54}N_{12}O_{15}S_4Pd_4$	$C_{32}H_{58}N_{10}O_{15}F_6Si_1S_4Pd_4$	$(C_{36}H_{70}N_9O_{14}F_9Si_{1.5}S_4Pd_4)_2$
F_w	1380.61	1400.69	1518.78	3239.91
Cryst dimens/mm	0.50 × 0.30 × 0.25	0.15 × 0.18 × 0.18	0.40 × 0.50 × 0.55	0.30 × 0.60 × 0.60
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	12.295(2)	13.649(3)	13.666(4)	18.037(6)
b/Å	28.358(2)	16.462(3)	22.599(5)	20.230(8)
c/Å	13.350(1)	12.527(3)	16.761(3)	17.802(6)
α/deg		105.09(2)		106.25(3)
β/deg	99.970(9)	111.06(2)	92.22(2)	107.20(3)
γ/deg		100.84(2)		100.85(3)
V/Å^3	4584.3(7)	2408(1)	5172(1)	5691(3)
Z	4	2	4	2
D_{calcd}/g cm^{-3}	2.000	1.931	1.950	1.890
μ/cm^{-1}	18.08	17.19	16.46	15.18
Transm factor	0.87—1.00	0.94—1.00	0.76—1.00	0.56—1.00
Scan type	ω-2θ	ω-2θ	ω-2θ	ω-2θ
2θ range/deg	55.3	55.0	55.0	55.0
No. of reflcns measd	11241	11518	12682	27408
No. of reflcns used	8217	6937	7769	15098
No. of variables used	568	592	637	1372
R (R_w)	0.028 (0.046)	0.038 (0.050)	0.050 (0.068)	0.060 (0.074)

thermal parameters of the non-hydrogen atoms in $\mathbf{1}(NO_3)_4\cdot 5H_2O$, $\mathbf{2}(NO_3)_4\cdot 3H_2O$, $\mathbf{3}(NO_3)_2SiF_6\cdot 9H_2O$, and $\mathbf{4}(NO_3)(SiF_6)_{1.5}\cdot 11H_2O$. The hydrogen atoms on the ligands were fixed by the geometrical and thermal constrains (C–H = N–H = 0.95 Å and U = 1.3 U (C, N). All of the calculations were performed on an Indigo II computer using teXsan.[23] The final atomic positional parameters are deposited in Tables S1—S12.[24] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 145585-145587.

Results and Discussion

Syntheses. The reaction of $[Pd(NO_3)_2(bpy)]$ with $[Pd(aet)_2]$ gave an S-bridged tetranuclear complex, $[\{Pd(bpy)\}_2\{Pd(aet)_2\}_2]^{4+}$ (**1**), in which two {Pd(bpy)} moieties take an intramolecular stacking arrangement. Similar reactions using $[Pd(NO_3)_2(diimine)]$ (diimine = dmbpy (**2**), phen (**3**), dmphen (**4**)) instead of $[Pd(NO_3)_2(bpy)]$ also gave $[\{Pd(diimine)\}_2\{Pd(aet)_2\}_2]^{4+}$-type tetranuclear complexes composed of square-planar Pd(II) units. On the other hand, the mononuclear complex $[Ni(aet)_2]$ reacts with $[PtCl_2(bpy)]$ to form another type of dinuclear complex, $[Pt(bpy)\{Ni(aet)_2(H_2O)_2\}]^{2+}$, in which the Ni(II) ion is converted from the square-planar coordination geometry to the octahedral one.[20] These facts indicate that $[Pd(aet)_2]$ is structurally more stable than $[Ni(aet)_2]$, and can function as a suitable spacer between two square-planar stacking units. Further, the formations of $[\{Pd(diimine)\}_2\{Pd(aet)_2\}_2]^{4+}$-type complexes imply that interactions between the π-electronic systems of the ligands significantly affect aggregations for polynuclear complexes.

X-Ray Crystal Structures. A perspective drawing of the complex cation **3** as a representative example for the present tetranuclear complexes is given in Fig. 1, and the selected bond distances and angles of **1**—**4**, are listed in Table 2. Here, the crystal of $\mathbf{4}(NO_3)(SiF_6)_{1.5}\cdot 11H_2O$ contains two independent tetravalent complex cations, two nitrate and three hexafluorosilicate anions, and twenty-two water molecules. However, both of the independent tetravalent complex cations are structurally identical with each other.

All of the complex cations **1**—**4** take similar structures, as represented by Fig. 1. Namely, these complex cations contain two square-planar {Pd(diimine)} moieties and two $[Pd(aet)_2]$ units to form S-bridged tetranuclear structures. Each of two Pd atoms in the {Pd(diimine)} moieties is bridged by two S atoms from two different $[Pd(aet)_2]$ units to allow two {Pd(diimine)} planes to be overlapped and parallel to each other, and the interplane distances between the least squares planes of two {Pd(diimine)} moieties are 3.443(5) Å for **1**, 3.58(1) Å for **2**, 3.39(1) Å for **3**, and 3.43(1) Å for **4**,

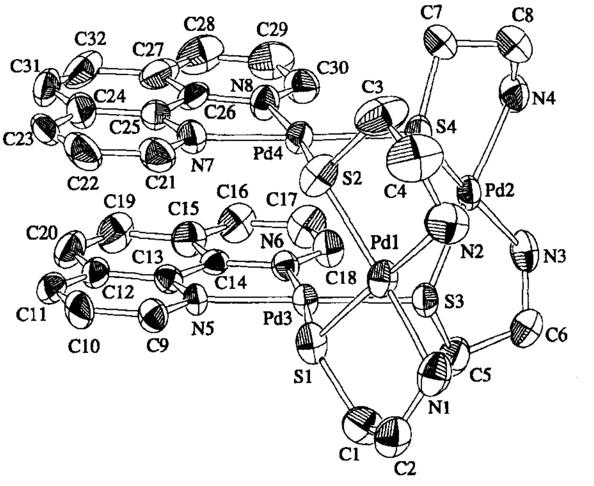

Fig. 1. Perspective view of $[\{Pd(phen)_2\}\{Pd(aet)_2\}_2]^{4+}$ (**3**) with the atomic labeling scheme.

Table 2. Selected Bond Distances (Å) and Angles (deg) of $[\{\mathrm{Pd(diimine)_2}\}\{\mathrm{Pd(aet)_2}\}_2]^{4+}$ (diimine = bpy (**1**), dmbpy (**2**), phen (**3**), dmphen (**4**))

	1	**2**	**3**	**4A**	**4B**
Pd(1)–S(1)	2.2774(9)	2.273(2)	2.281(2)	2.277(2)	2.259(3)
Pd(1)–S(2)	2.2832(9)	2.284(2)	2.272(2)	2.289(2)	2.285(2)
Pd(1)–N(1)	2.066(3)	2.065(5)	2.059(6)	2.072(7)	2.067(8)
Pd(1)–N(2)	2.079(3)	2.070(5)	2.068(6)	2.064(7)	2.055(7)
Pd(2)–S(3)	2.2711(9)	2.263(2)	2.265(2)	2.260(2)	2.270(2)
Pd(2)–S(4)	2.2620(9)	2.265(1)	2.269(2)	2.269(2)	2.257(3)
Pd(2)–N(3)	2.065(3)	2.083(4)	2.090(6)	2.072(7)	2.079(8)
Pd(2)–N(4)	2.086(3)	2.068(5)	2.093(6)	2.070(7)	2.069(8)
Pd(3)–S(1)	2.2934(8)	2.290(2)	2.283(2)	2.289(2)	2.271(2)
Pd(3)–S(3)	2.3022(9)	2.296(1)	2.287(2)	2.278(2)	2.316(2)
Pd(3)–N(5)	2.094(3)	2.072(4)	2.103(4)	2.067(5)	2.098(7)
Pd(3)–N(6)	2.073(3)	2.070(5)	2.090(5)	2.069(6)	2.080(6)
Pd(4)–S(2)	2.2870(9)	2.296(2)	2.277(2)	2.296(2)	2.295(2)
Pd(4)–S(4)	2.2872(9)	2.297(2)	2.287(2)	2.292(2)	2.283(2)
Pd(4)–N(7)	2.085(3)	2.069(4)	2.080(5)	2.093(5)	2.084(6)
Pd(4)–N(8)	2.091(3)	2.078(5)	2.090(5)	2.086(6)	2.079(6)
S(1)–Pd(1)–S(2)	94.61(3)	94.61(6)	95.55(7)	94.27(8)	94.75(9)
S(1)–Pd(1)–N(1)	85.94(10)	85.7(1)	86.1(2)	86.0(2)	85.5(2)
S(1)–Pd(1)–N(2)	174.75(9)	174.2(1)	177.9(2)	176.5(2)	174.8(2)
S(2)–Pd(1)–N(1)	178.28(9)	177.2(1)	172.9(2)	177.0(2)	175.8(2)
S(2)–Pd(1)–N(2)	86.28(9)	86.5(1)	86.2(2)	86.8(2)	86.9(2)
N(1)–Pd(1)–N(2)	93.0(1)	92.9(2)	92.1(3)	92.9(3)	92.5(3)
S(3)–Pd(2)–S(4)	93.80(3)	93.54(5)	92.98(6)	95.54(8)	94.32(9)
S(3)–Pd(2)–N(3)	85.75(10)	85.8(2)	85.8(2)	85.8(2)	86.6(2)
S(3)–Pd(2)–N(4)	176.14(9)	173.4(2)	175.2(2)	174.9(2)	176.2(2)
S(4)–Pd(2)–N(3)	172.42(9)	175.8(2)	173.1(2)	175.6(2)	174.5(2)
S(4)–Pd(2)–N(4)	86.03(10)	86.2(1)	85.3(2)	86.2(2)	86.5(2)
N(3)–Pd(2)–N(4)	93.9(1)	93.9(2)	95.4(2)	92.1(3)	92.3(3)
S(1)–Pd(3)–S(3)	87.13(3)	86.39(5)	87.98(6)	87.59(8)	88.12(9)
S(1)–Pd(3)–N(5)	92.52(8)	92.8(1)	92.3(1)	92.6(2)	90.0(2)
S(1)–Pd(3)–N(6)	172.01(8)	171.4(1)	172.1(1)	172.0(2)	170.0(2)
S(3)–Pd(3)–N(5)	171.83(8)	179.1(1)	179.7(1)	172.7(2)	175.7(2)
S(3)–Pd(3)–N(6)	100.80(8)	102.0(1)	99.7(1)	99.6(2)	101.9(2)
N(5)–Pd(3)–N(6)	79.5(1)	78.8(2)	80.1(2)	80.6(2)	80.1(2)
S(2)–Pd(4)–S(4)	86.38(3)	85.75(5)	86.98(7)	86.13(7)	86.68(8)
S(2)–Pd(4)–N(7)	93.37(8)	94.4(1)	91.5(2)	93.7(2)	94.0(2)
S(2)–Pd(4)–N(8)	171.69(8)	173.5(1)	171.4(1)	171.2(2)	172.9(2)
S(4)–Pd(4)–N(7)	175.25(8)	176.8(1)	177.0(2)	177.8(2)	178.4(2)
S(4)–Pd(4)–N(8)	101.39(8)	100.7(1)	101.6(1)	100.8(2)	100.2(2)
N(7)–Pd(4)–N(8)	79.1(1)	79.1(2)	79.9(2)	79.5(2)	79.2(2)
Pd(1)–S(1)–Pd(3)	117.32(4)	108.97(7)	114.80(8)	108.08(9)	113.5(1)
Pd(1)–S(2)–Pd(4)	111.12(4)	111.26(4)	113.77(8)	112.62(9)	112.85(10)
Pd(2)–S(3)–Pd(3)	121.08(4)	120.51(7)	111.43(7)	120.03(9)	120.5(1)
Pd(2)–S(4)–Pd(4)	112.46(4)	114.25(6)	119.63(8)	113.82(9)	113.55(9)

respectively. This indicates that the π-electronic systems of two {Pd(diimine)} moieties in these complex cations can interact with each other. The interplane distances of the phen complexes (**3** and **4**) are considerably shorter than those of the bpy complexes (**1** and **2**). This suggests that the π-electronic systems in the former more strongly interact than those in the latter. Furthermore, the distances in **2** and **4** are significantly longer than those in **1** and **3**, respectively, reflecting the introductions of the methyl groups. The $\mathrm{PdN_2S_2}$ planes in the $[\mathrm{Pd(aet)_2}]$ units are almost perpendicular to those in the {Pd(diimine)} moieties, and the Pd–S–Pd bridging angles (av 115.50(4)° for **1**, av 113.75(7)° for **2**, av 114.91(8)° for **3**, and av 114.4(1)° for **4**) are similar to those observed in $[\mathrm{Pd_2}\{\mathrm{Pd(aet)_2}\}_4]^{4+}$.[14] These angles are slightly different from each other, and the angles of the dimethyl-substituted derivatives are relatively more acute than those of the corresponding non-substituted derivatives.

Projection of crystal packing for **1**—**3** are shown in Figs. 2, 3, and 4, respectively. As shown in Fig. 2, one vacant axial site of the Pd atom in one {Pd(bpy)} moiety in **1** is occupied by a oxygen atom of nitrate anion (Pd–O = 3.055(4) Å), but that in the other {Pd(bpy)} moiety is not occupied. As a result, the π-electronic system of one {Pd(bpy)} moiety can interact with that in an adjacent complex cation to

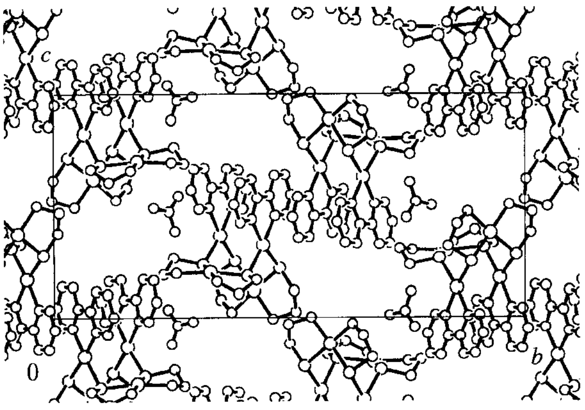

Fig. 2. Projection of crystal packing for $[\{Pd(bpy)_2\}\{Pd(aet)_2\}_2](NO_3)_4 \cdot 5H_2O$ ($\mathbf{1}(NO_3)_4 \cdot 5H_2O$) viewed along *a* axis.

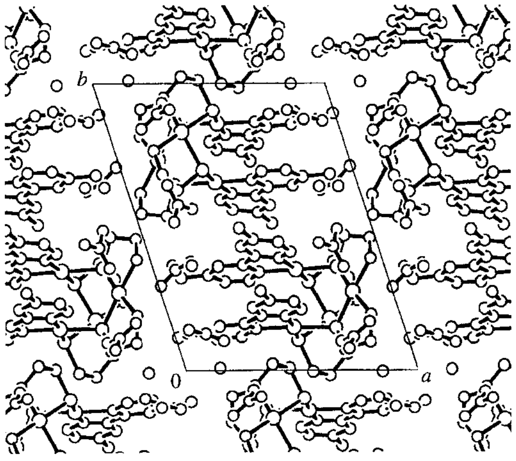

Fig. 3. Projection of crystal packing for $[\{Pd(dmbpy)_2\}\{Pd(aet)_2\}_2](NO_3)_4 \cdot 3H_2O$ ($\mathbf{2}(NO_3)_4 \cdot 3H_2O$) viewed along *c* axis.

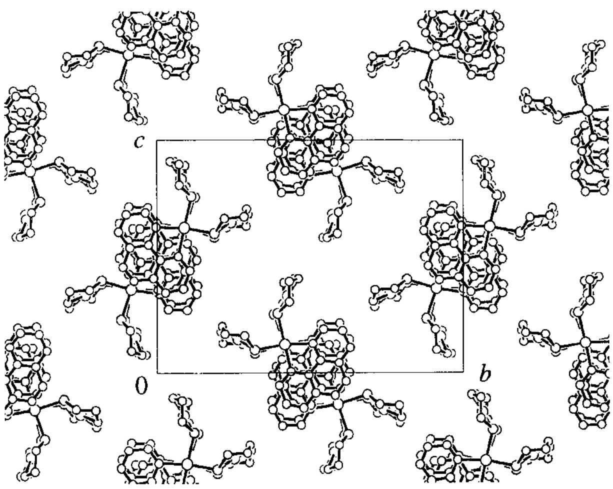

Fig. 4. Projection of crystal packing for $[\{Pd(phen)_2\}\{Pd(aet)_2\}_2](NO_3)_2SiF_6 \cdot 9H_2O$ ($\mathbf{3}(NO_3)_2SiF_6 \cdot 9H_2O$) viewed along *a* axis.

take a dimeric structure in the crystalline state. This is supported by the interplane distance (3.528(5) Å) between two least squares planes of the neighboring {Pd(bpy)} moieties within the range of the π-π stacking contact (Table 3).[17] Similarly, **2** takes a dimeric structure due to intermolecular π-π stacking between two {Pd(dmbpy)} moieties (the interplane distance = 3.621(8) Å). Contrary to the case of **1**, however, no axial vacant sites of {Pd(dmbpy)} in **2** are occupied by nitrate anions or water molecules (Fig. 3). This may imply that these dimeric structures for **1** and **2** are caused by the extent of π-electronic systems in bpy skeletons. On the other hand, **3** and **4** exist in the linear-chain-like structures with alternate coplanar stacking arrangements (Fig. 4), which are in contrast to the intermolecular structures for **1** and **2**. Namely, one {Pd(phen)} or {Pd(dmphen)} moiety in the complex cation is overlapped with a {Pd(phen)} or {Pd(dmphen)} moiety in the neighboring complex cation. Further, another {Pd(phen)} or {Pd(dmphen)} moiety in the complex cation approaches to a {Pd(phen)} or {Pd(dmphen)} moiety in the other neighboring complex cation. Therefore, the interplane distances (av 3.40(1) Å for **3** and av 3.57(1) Å for **4**) between two least squares planes of the neighboring {Pd(diimine)} moieties are also within the range of the π-π stacking contact (Table 3).[17] Thus, similar trends to the case of intramolecular interplane distances are observed for these intermolecular interplane distances. Namely, the interplane distances of the bpy complexes (**1** and **2**) are considerably longer than those of the phen complexes (**3** and **4**), and the distances in dimethyl-substituted derivatives (**2** and **4**) are significantly longer than those in the corresponding non-substituted derivatives (**1** and **3**). These are reflected by the differences in the extent of π-electronic systems and the steric factors between the diimine ligands.

Characterization. The electronic absorption and diffuse reflection spectra of $\mathbf{1}(NO_3)_4 \cdot 5H_2O$ are shown in Fig. 5. Further, the absorption and reflection spectral data of the complex, together with those of $\mathbf{2}(NO_3)_4 \cdot 3H_2O$, $\mathbf{3}(NO_3)_4 \cdot 3H_2O$, and $\mathbf{4}(NO_3)_4 \cdot 3H_2O$, are summarized in Table 4. Here, the electronic absorption and diffuse reflection spectra of $\mathbf{3}(NO_3)_4 \cdot 3H_2O$ and $\mathbf{4}(NO_3)_4 \cdot 3H_2O$ were almost identical with those of $\mathbf{3}(NO_3)_2SiF_6 \cdot 9H_2O$ and $\mathbf{4}(NO_3)(SiF_6)_{1.5} \cdot 11H_2O$, respectively. This implies, in both solid state and solution, that the structures of $\mathbf{3}(NO_3)_4 \cdot 3H_2O$ and $\mathbf{4}(NO_3)_4 \cdot 3H_2O$ can be regarded as identical with those of $\mathbf{3}(NO_3)_2SiF_6 \cdot 9H_2O$ and $\mathbf{4}(NO_3)(SiF_6)_{1.5} \cdot 11H_2O$, respectively. Accordingly, the electronic absorption and diffuse reflection spectral data were summarized only for the nitrate salts of **3** and **4**. As shown in Fig. 5, **1** exhibits three

Table 3. Intra- and Intermolecular Interplane Distances (Å) between the Least Squares Planes of Two $[\{Pd(diimine)_2\}\{Pd(aet)_2\}_2]^{4+}$ (diimine = bpy (**1**); dmbpy (**2**); phen (**3**); dmphen (**4**))

	Intramolecular	Intermolecular
$[\{Pd(bpy)_2\}\{Pd(aet)_2\}_2]^{4+}$ (**1**)	3.443(5)	3.528(5)
$[\{Pd(dmbpy)_2\}\{Pd(aet)_2\}_2]^{4+}$ (**2**)	3.58(1)	3.621(8)
$[\{Pd(phen)_2\}\{Pd(aet)_2\}_2]^{4+}$ (**3**)	3.39(1)	3.40(1)[a]
$[\{Pd(dmphen)_2\}\{Pd(aet)_2\}_2]^{4+}$ (**4**)	3.43(1)	3.57(1)[a]

a) averaged.

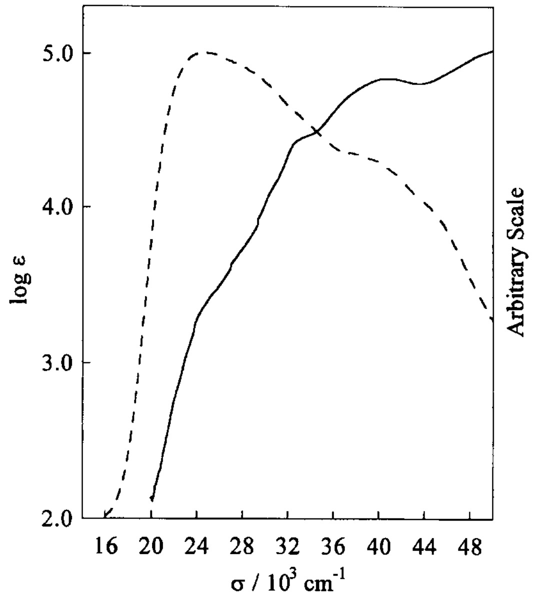

Fig. 5. Electronic absorption (—; log ε) and diffuse reflection spectra (····) of [{Pd(bpy)$_2$}{Pd(aet)$_2$}$_2$](NO$_3$)$_4$·5H$_2$O (**1**(NO$_3$)$_4$·5H$_2$O).

peaks at 33.28, 41.84, and 49.75×10^3 cm^{-1}, and two shoulders around 25.0 and 30.3×10^3 cm^{-1} in water. Among these bands, the 30.3×10^3 cm^{-1} band is assigned as a d-d transition due to Pd^{2+} ions, and the 33.28×10^3 cm^{-1} band is ascribed to the π–π* transition localized on the bpy skeleton.[22,25,26] On the other hand, the bands at 41.84 and 49.75×10^3 cm^{-1} can be regarded as charge-transfer (CT) bands from sulfur to palladium. Although the band corresponding to the 25.0×10^3 cm^{-1} band is not observed in the spectrum of [Pd$_2${Pd(aet)$_2$}$_4$]$^{4+}$,[14] similar bands are observed for the other tetranuclear complexes **2**—**4** (Table 4). It is considered, therefore, that the bands around 25.0×10^3 cm^{-1} are characteristic for the present [{Pd(diimine)}$_2${Pd(aet)$_2$}$_2$]$^{4+}$-type complexes. In the diffuse reflection spectrum of **1**, the 25.0, 30.3, 41.84, and 49.75×10^3 cm^{-1} bands in water are shifted to the lower-energy-side and appear at 24.54, 28.0, 37.74, and 46.5×10^3 cm^{-1}. On the other hand, the 33.28×10^3 cm^{-1} band due to the π-π* transition localized on bpy skeleton is slightly shifted to the higher-energy-side and appears at 33.6×10^3 cm^{-1}. Similar trends are also observed for the other tetranuclear complexes **2**—**4**. It is suggested, accordingly, that these higher-energy-side shifts may be reflected by differences in the inter- and/or intramolecular interactions around the diimine skeleton between in solution and in the solid state.

The ^{13}C NMR spectrum of **1** exhibits two signals at δ = 38.42, 50.29, 126.46, 130.99, 144.75, 151.67, and 157.39. Among these signals, the signals at 38.42 and 50.29 are assigned to the carbon atoms of –CH$_2$S groups and –CH$_2$N groups in aet, respectively. The ^{13}C NMR spectrum for the carbon atoms in bpy skeletons consists of five independent signals (δ = 126.46, 130.99, 144.75, 151.67, and 157.39), in spite of twenty carbons in two bpy skeletons. A similar trend is also observed for the hydrogen atoms in bpy skeletons in the ^{1}H NMR spectrum, namely, four independent signals for sixteen hydrogen atoms. These indicate that no intermolec-

Table 4. Absorption and Reflection Spectral Data of [{Pd(diimine)$_2$}{Pd(aet)$_2$}$_2$](NO$_3$)$_4$·nH$_2$O (diimine = bpy, n = 5 (**1**); dmbpy, n = 3 (**2**); phen, n = 3 (**3**); dmphen, n = 3 (**4**))

	Absorption maxima σ/10^3 cm^{-1} (ε/10^3 mol^{-1} dm^3 cm^{-1})	Reflection maxima σ/10^3 cm^{-1}
[{Pd(bpy)$_2$}{Pd(aet)$_2$}$_2$]$^{4+}$ (**1**)	25.0 (3.2)^{sh}	24.54
	30.3 (12.4)^{sh}	28.0^{sh}
	33.28 (26.96)	33.6^{sh}
	41.84 (61.82)	37.74
	49.75 (101.3)	46.5^{sh}
[{Pd(dmbpy)$_2$}{Pd(aet)$_2$}$_2$]$^{4+}$ (**2**)	25.8 (3.1)^{sh}	24.57
	30.9 (14.1)^{sh}	28.4^{sh}
	33.0 (32.0)^{sh}	34.0^{sh}
	39.60 (101.98)	37.6^{sh}
	47.1 (102.6)^{sh}	44.4^{sh}
[{Pd(phen)$_2$}{Pd(aet)$_2$}$_2$]$^{4+}$ (**3**)	25.4 (3.3)^{sh}	24.42
	32.8 (20.2)^{sh}	29.1^{sh}
	38.46 (60.77)	39.1^{sh}
	47.0 (114.4)^{sh}	44.7^{sh}
	49.75 (128.85)	48.8^{sh}
[{Pd(dmphen)$_2$}{Pd(aet)$_2$}$_2$]$^{4+}$ (**4**)	24.7 (2.4)^{sh}	24.18
	32.1 (17.0)^{sh}	29.4^{sh}
	36.67 (63.93)	37.59
	46.9 (112.7)^{sh}	45.0^{sh}
	48.54 (123.39)	47.8^{sh}

The sh label denotes a shoulder.

ular π–π interactions in the present conditions, namely, concentration of 10^{-2} mol dm^{-3} at room temperature. It is considered, furthermore, that no intramolecular interactions may exist between the two π-electronic systems of the bpy skeletons, because only five ^{13}C NMR signals and four ^{1}H NMR signals are observed for two bpy skeletons, which imply that four pyridyl rings are almost equivalent with each other. This is supported by the fact that these signals are located at almost the same positions as the other complex including only one {Pd(bpy)} moiety.[26] Similar trends are also observed for other three tetranuclear complexes, indicating no intra- and intermolecular π-π interactions between two π-electronic systems in the diimine moieties of **2**, **3**, and **4** in solution.

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